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A SPECTROSCOPIC STUDY OF THE CHEMILUMINESCENT REACTION OF GERMANE WITH ATOMIC OXYGEN

A. SHARMA

J. P. PADUR



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A SPECTROSCOPIC STUDY OF THE CHEMILUMINESCENT REACTION OF GERMANE WITH ATOMIC OXYGEN

By A. Sharma and J. P. Padur
GCA Corporation, GCA Technology Division

INTRODUCTION

The spectroscopic study of the chemiluminescent reactions of atomic oxygen with different substances has been previously undertaken and summarized by Gaydon [1]*. Recently, Kaufman [2] has reviewed the work on the kinetics of atomic oxygen reactions. The chemiluminescent reactions of atomic oxygen with some hydrocarbons [3], nitric oxide [4] and carbon monoxide [5] have been studied in this laboratory. No information regarding the chemiluminescent reaction of atomic oxygen with germanium compounds is available. We have found that the mixing of germanium tetrahydride with atomic oxygen is accompanied by a strong blue chemiluminescence. However, the mixing of germanium tetrachloride with atomic oxygen does not produce any chemiluminescence. The examination of the spectra of the chemiluminescence produced during the reaction of germanium tetrahydride reveals the presence of large numbers of bands from 2450Å to 5100Å. Most of the bands on the more refrangible side of the spectrum belongs to the D-X system and the presence of a new band system on the longer wavelength side is indicated.

The spectrum of GeO has been previously observed by Shaw [6] and SenGupta [7] in emission from a carbon arc containing germanium compounds. The D-X system of GeO was extended by Jevons, et al., [8] who studied the GeO spectrum in emission from an electric discharge through flowing vapor of germanium tetrachloride and oxygen. The spectrum obtained by us is comparatively free from the presence of other spectral features which usually complicates the discharge or arc spectrum. Therefore, we have been able to observe a number of new bands belonging to the D-X system. The present study shows that the spectroscopic study of the chemiluminescent reactions of atomic oxygen can reveal more information about the spectra of diatomic oxides than from conventional sources. This is due to the fact that 'cold' chemiluminescent reactions are low temperature sources which give better contrast between the band and the overlying structure of the neighboring bands. Moreover, due to the selective excitation of some band systems, the observed spectrum is free from the presence of other features. Consequently the observed band system can be extensively studied. The results of the spectroscopic study of the chemiluminescent reaction between germane and atomic oxygen are given here.

*Numbers in [] throughout the text represent reference numbers.

EXPERIMENTAL

A conventional fast flow system suitable for the 1 mm pressure region was used for the present study. The apparatus manifold is shown in schematic form in Figure 1. Atomic oxygen was produced by a microwave discharge through about 100 : 1 mixture of argon and oxygen, which provided a sufficient concentration of atomic oxygen in the presence of a small concentration of molecular oxygen. The flow tube dimensions were such that the linear velocities of gases were of the order of 1000 cm/sec. Therefore, the depletion of atomic oxygen due to recombination between the discharge and point of mixing was very small. The germanium tetrahydride and germanium tetrachloride were obtained from Alfa Inorganics and were admixed with the stream of atomic oxygen in a 2 cm i.d. pyrex tube equipped with quartz windows for observation of UV spectra. It has been reported [9] that the relative intensity of different spectral features observed in the chemiluminescent reaction of acetylene and atomic oxygen is different at different distances from the point of mixing. Therefore, one quartz window was provided at the point of mixing and another at some distance from it. The reaction tube is shown in Figure 2.

The preliminary spectra were recorded by a Perkin Elmer (Model 99) monochromator equipped with 600 lines/mm grating blazed for 5000Å and an E.M.1 9558Q photomultiplier tube. The spectra were recorded at both windows and no remarkable difference between them was found. This is due to the fact that most of the observed spectral features are due to GeO molecules alone. On the other hand the observed features in the spectrum of chemiluminescence produced during the reaction of acetylene and atomic oxygen are due to different species, e.g. C₂, CH, and OH. The relative rate of excitation may be different for each of the above species at different distances from the point of mixing.

The spectral response of the recording system employed was calibrated with a standard light source (GE quartz iodine tungsten filament lamp, Model 6.6A/T4Q/1CL-200 W). The absolute irradiance of the lamp was obtained from Stair, et al. [10]. The corrected profile of the recorded spectra is shown in Figure 3, which indicates that the radiation is predominantly emitted in the region around 3100Å. Since the sensitivity of the recording system drops considerably at shorter wavelength, the spectra of the chemiluminescence was photographed with a Hilger small quartz spectrograph. The recorded spectrum is shown in Plate 1. It may be noted that this spectrum shows the presence of extensive bands from 2500Å to 5100Å.

The dispersion and resolution of the small quartz spectrograph was not sufficient for the definite identification of spectral features. Therefore, the final spectrum was recorded with a 1.5 m Jarrel Ash grating spectrograph with a grating blazed at 3000Å and reciprocal dispersion of about 11 Å/mm. 103 a-F films were used with an exposure time of about 2 hours. As compared with other common spectroscopic sources, the intensity of chemiluminescence produced during the reaction of germane with atomic oxygen was low. Consequently, a comparatively wider slit was used for recording the spectrum.

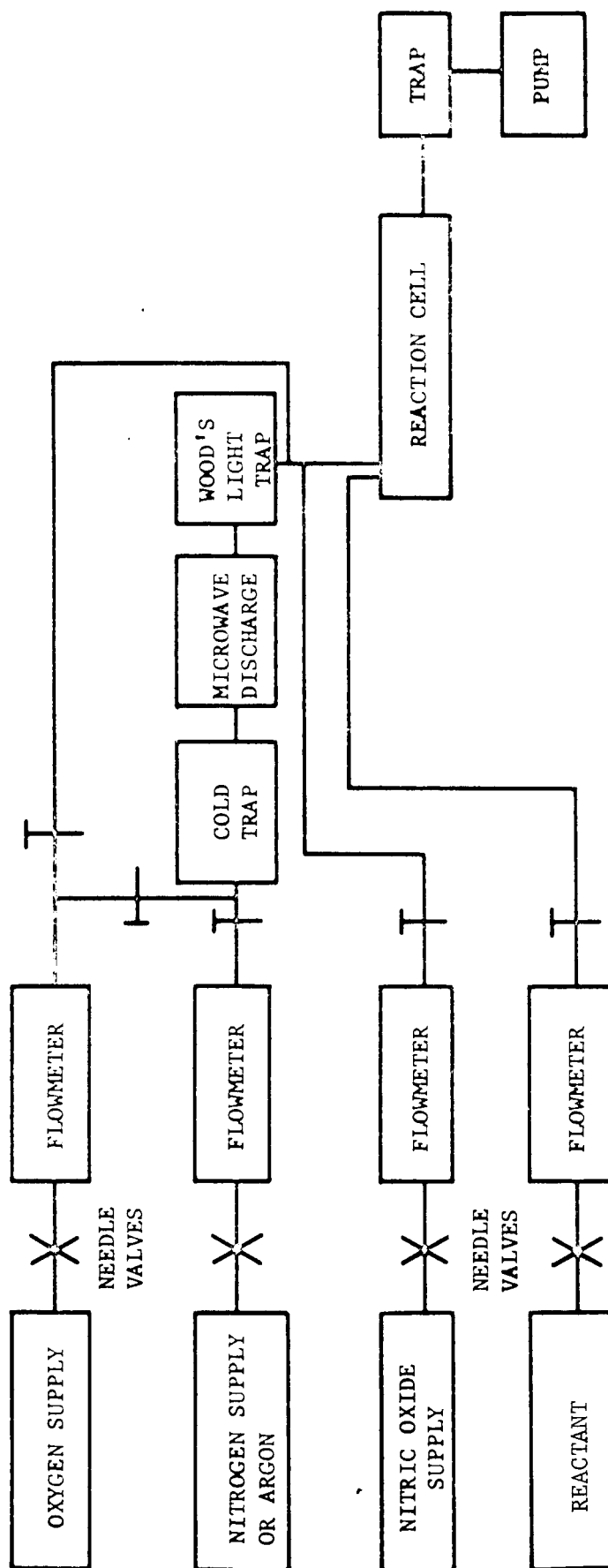


Figure 1. Block diagram of apparatus for observing chemiluminescence.

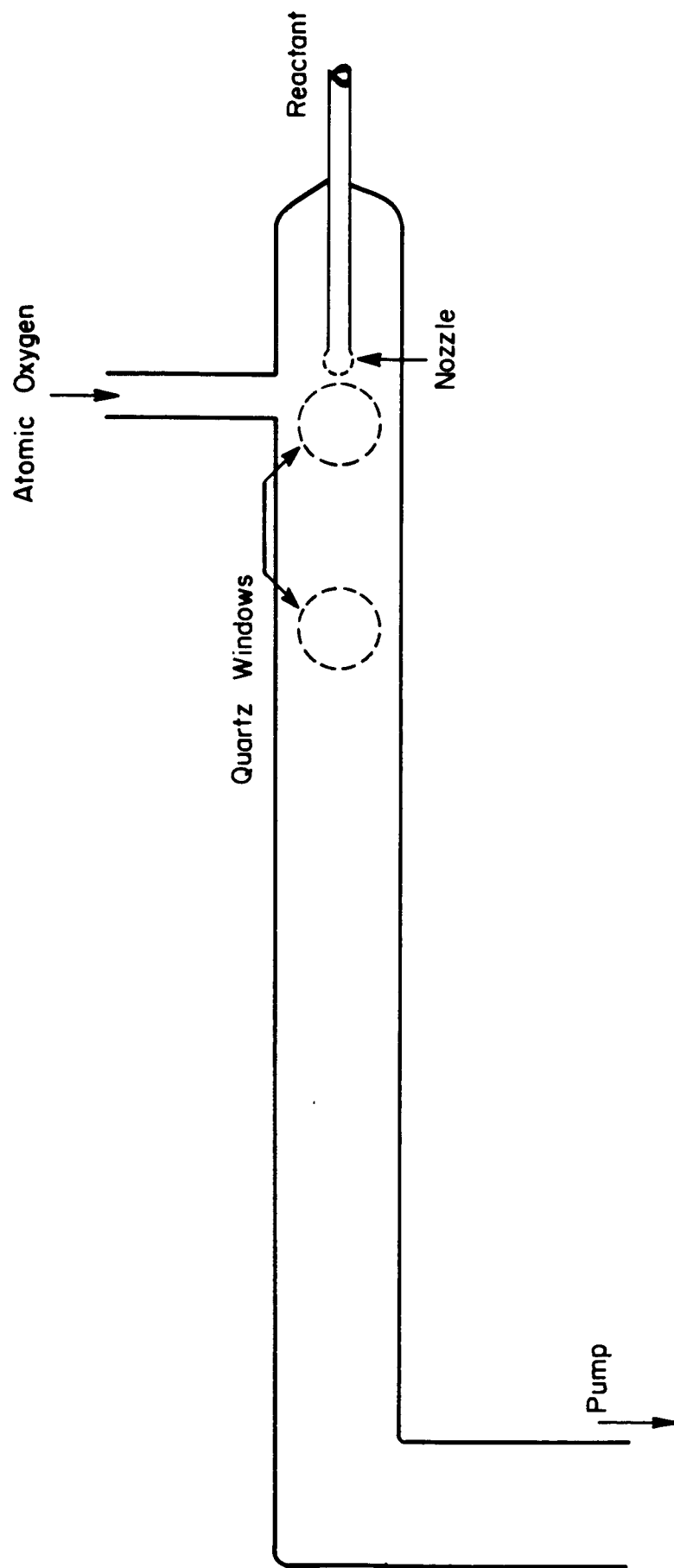


Figure 2. Reaction tube.

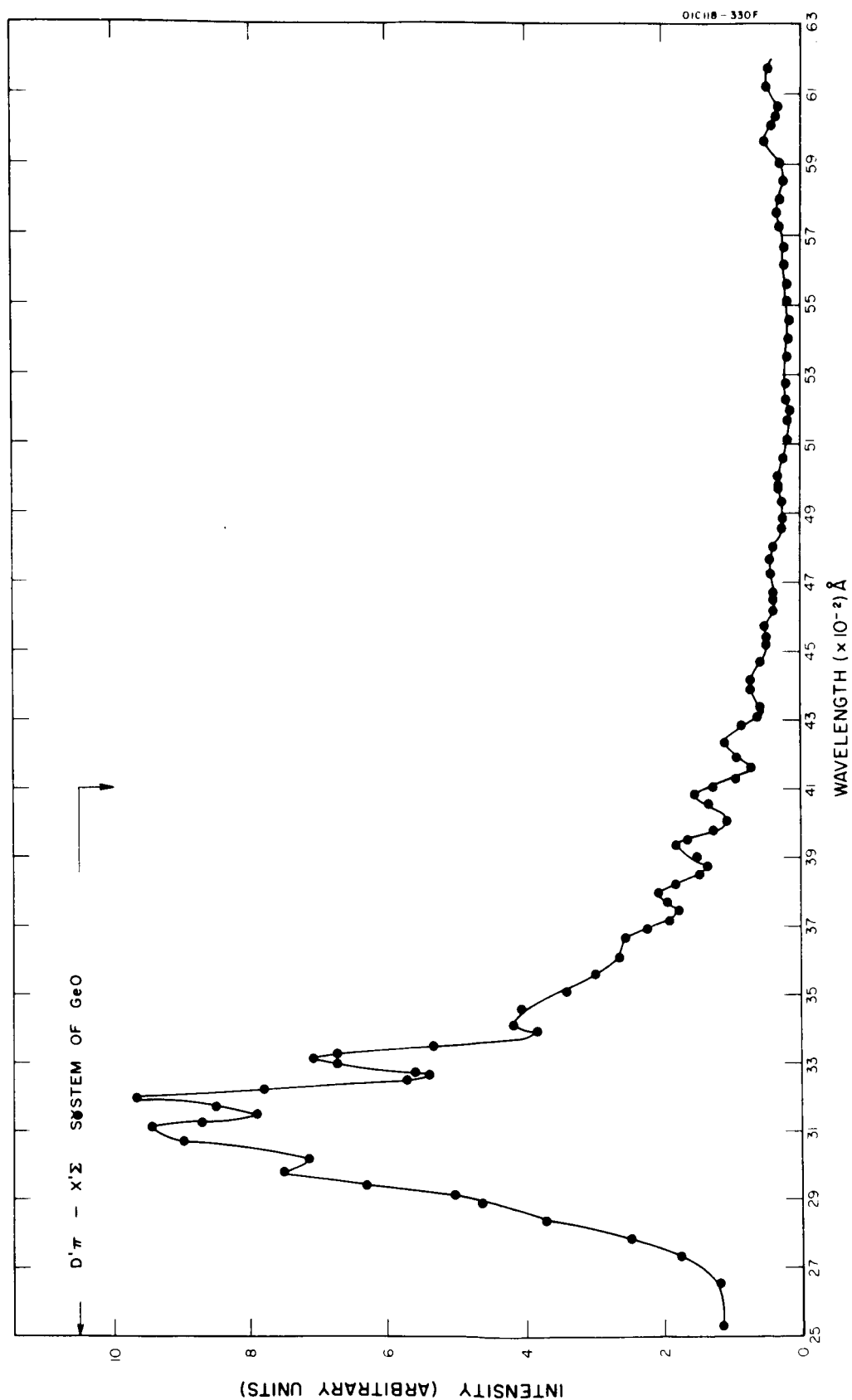


Figure 3. The spectrum of the chemiluminescent reaction of germane with atomic oxygen.

THE SPECTRUM OF CHEMILUMINESCENCE PRODUCED DURING THE REACTION
OF GERMANE WITH ATOMIC OXYGEN.

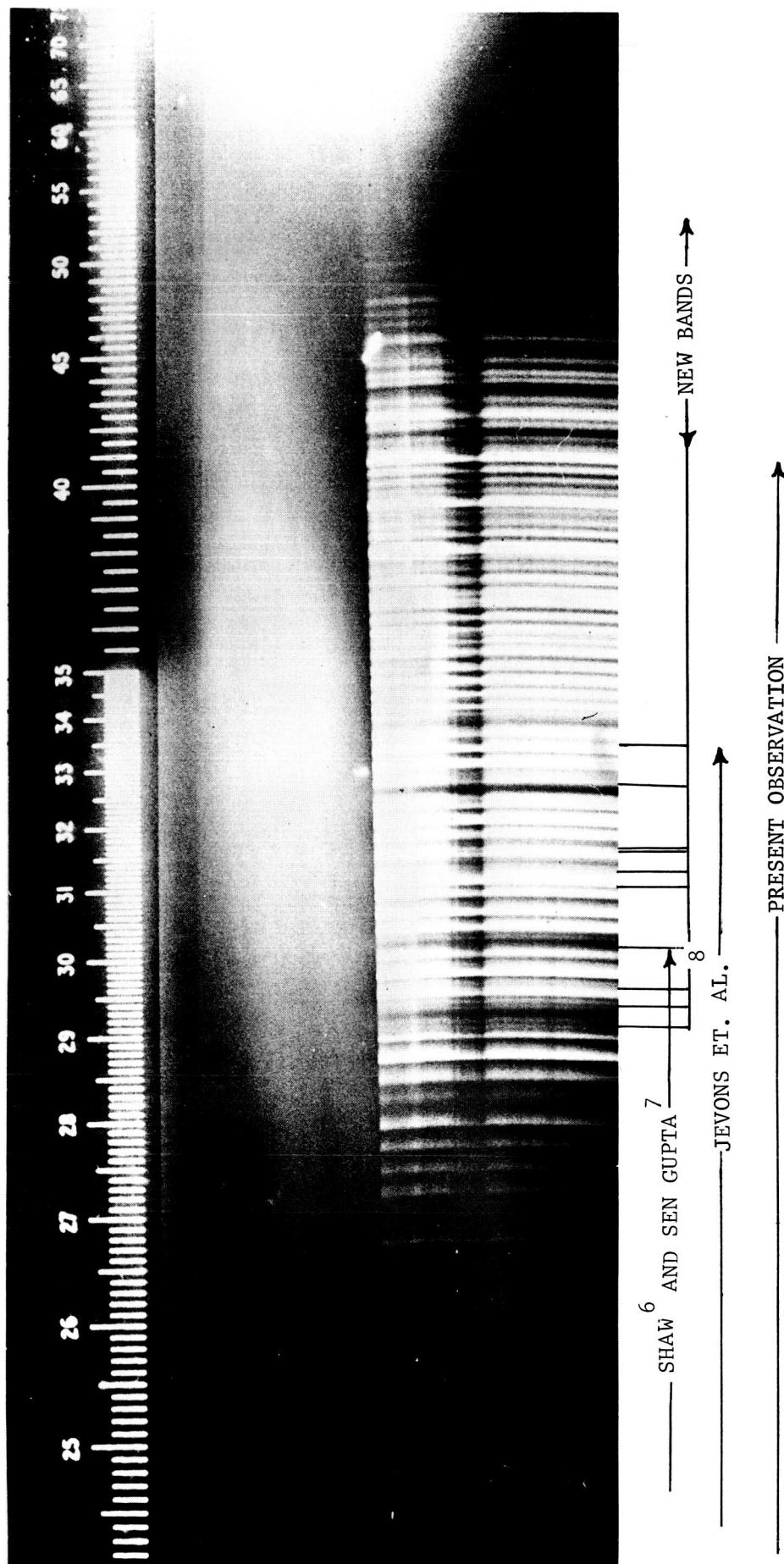


PLATE 1- Spectra photographed on small quartz spectrograph.
The extension of D - X system of GeO by different
observers is indicated.

This has necessarily resulted in some loss of resolution. The recorded spectrum is shown in Plate 2.

MEASUREMENT AND INTERPRETATION

The spectrum recorded with the 1.5 m grating spectrograph was used for the measurement of the band heads. Most of the observed bands are degraded to the red. Due to the wide slit width the degradation of some of the observed bands is uncertain. The wavelength and visually estimated intensities of the observed band heads are given in Table 1. The spectrum of the chemiluminescence is extensive and consists of about one hundred bands between 2350Å and 4000Å. Most of the observed bands are degraded to longer wavelength and the measured wavelengths of some prominent bands agreed with bands belonging to the D-X system of GeO (the bands of the D-X system of GeO are also degraded to the red) given by Pearse and Gaydon [11]. The D-X system of GeO has been previously studied by Jevons et al., [8]. It was found that all the thirty bands listed by Jevons et al., [8] can be identified in the present spectrum. The wavelength of the GeO bands belonging to the D-X system measured by Jevons et al., [9] is given in column three of Table 1. Because of the similar appearance of the remaining bands and the same region of their appearance, it was suspected that the remaining bands may also belong to the D-X system of the GeO molecule. Therefore, the wavelengths of the bands of the above system with v' up to 10 and v'' up to 15 were calculated from the following expression given by Jevons et al., [8].

$$\nu = 37762.4 + (651.3u' - 4.20u'^2) - (985.7u'' - 4.30u''^2)$$

where $u = v + 1/2$. With the help of the calculated wavelength of the bands a number of remaining bands are identified. The calculated wavelengths of the identified bands together with the vibrational quantum numbers of the states involved in the transition are given in the fourth column of Table 1. It may be concluded from the table that most of the prominent bands observed in the spectrum of the chemiluminescence produced during the reaction of germane with the atomic oxygen belong to the D-X system of GeO. Considering the fact that a comparatively wider slit was used for recording the spectrum, the agreement between the calculated and measured wavelength of the identified bands is within experimental error.

The unique combination of w' and w'' ($3w' \approx 2w''$) has resulted in a narrow grouping of several bands, which together with the low resolution further complicates the identification of some bands. For example, the 3,5 band at 2881.95Å, 0,3 band at 288.71Å and 6,7 band at 2884.69Å lie very close to each other. A number of such cases are shown in Table 1. A number of bands which can not be identified definitely with the bands of the D-X system of GeO are collected in Table 2. The three strongest unidentified bands are at 3053.4Å, 3122.5Å and 3175.4Å. The observed unidentified features at 3122.5Å and 3175Å may be due to OH ultraviolet bands. However, this identification and assignment of remaining bands is not possible with the present spectrum.

THE SPECTRUM OF CHEMILUMINESCENCE PRODUCED DURING
THE REACTION OF GERMANE WITH ATOMIC OXYGEN

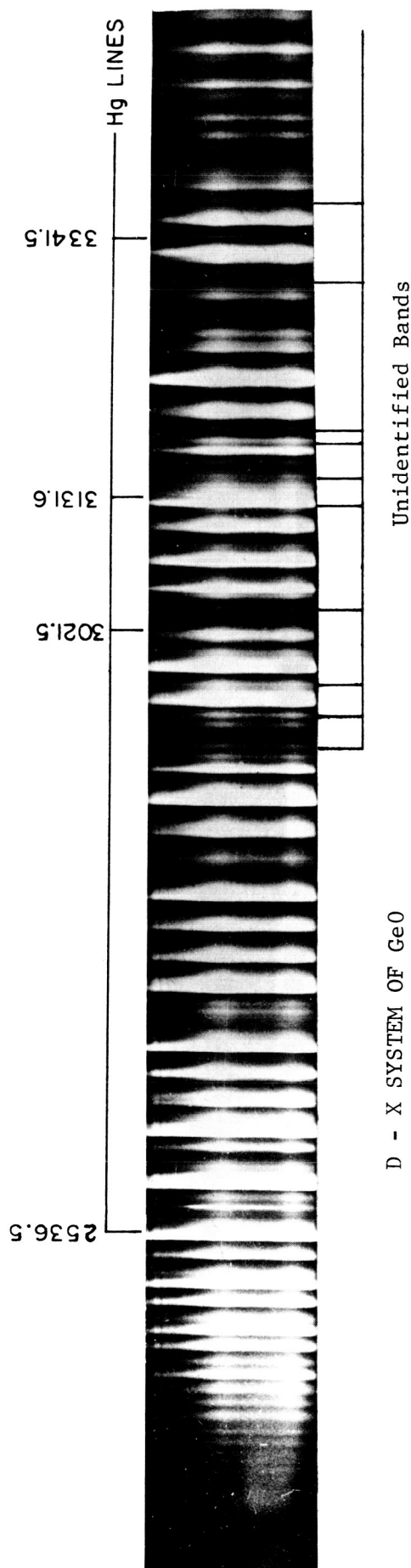


PLATE 2 - Spectra photographed on 1.5 m grating spectrograph. The unidentified bands are indicated.

TABLE 1
THE IDENTIFICATION OF THE BANDS OF D-X SYSTEM OF GeO

S. No.	Measured λ Å	Intensity Visual Estimate	λ , (u', u'') Jevons	Identification λ Calculated (V', V'')
1	2364.7*	1		2365.85 (11, 2)
2	2373.6*	1		2375.4 (9, 1)
3	2386.1*	2		2385.67 (7, 0)
4	2397.1*	2		2398.3 (10, 2)
5	2406.8*	2		2408.29 (8, 1)
6	2418.9*	6		2419.85 (6, 0)
7	2429.4*	1		2431.33 (9, 2)
8	2441.40	10	2441.9 (7, 1)	2442.61 (7, 1)
9	2454.0	12	2454.8 (5, 0)	2454.80 (10, 3), 2455.52 (5, 0)
10	2465.1*	4		2465.81 (8, 2)
11	2477.3	5	2477.8 (6, 1)	2478.45 (6, 1)
12	2491.5	18	2492.2 (4, 0)	2489.43 (9, 3), 2492.80 (4, 0)
13	2501.9*	2		2501.80 (7, 2)
14	2514.8	10	2514.88 (5, 1)	2513.50 (10, 4), 2515.89 (5, 1)
15	2530.0	30	2531.10 (3, 0)	2531.76 (3, 0)
16	2562.4*	1		2563.35 (7, 3)
17	2571.0	30	2511.83 (2, 0)	2572.52 (2, 0)
18	2587.6*	2		2587.76 (8, 4)
19	2602.8*	12		2602.85 (6, 3)
20	2613.5	30	2614.13 (1, 0)	2612.62 (9, 5), 2615.20 (1, 0)
21	2621.90	15	2619.5 (4, 2)	2619.36 (4, 2)
22	2627.8*	6		2627.4 (7, 4)
23	2638.0	12	2639.17 (2, 1)	2637.9 (10, 6), 2638.85 (2, 1)
24	2644.9*	12		2644.17 (5, 3)
25	2652.2*	1		2652.46 (8, 5)
26	2658.5	20	2659.42 (0, 0)	2659.90 (0, 0)
27	2661.1	20	2662.33 (3, 2)	2662.93 (3, 0)
28	2682.2	30	2682.98 (1, 1)	2683.78 (1, 1)
29	2713.4	4	2707.4 (2, 2)	2712.40 (5, 4)
30	2720.4*	2		2719.85 (8, 6)
31	2730.17	20	2730.02 (0, 1)	2730.90 (0, 1)
32	2754.6*	15		2755.4 (1, 2)
33	2780.1	15	2779.71 (2, 3)	2780.55 (2, 3)
34	2804.2	22	2804.17 (0, 2)	2805.09 (0, 2), 2805.73 (3, 4)
35	2837.4*	25		2836.25 (7, 7)
36	2845.9*	4		2844.3 (10, 9)
37	2856.2	15	2855.42 (2, 4)	2855.87 (2, 4), 2857.89 (5, 6)
38	2881.6	30	2881.75 (0, 3)	2881.95 (3, 5), 2882.71 (0, 3)
39	2893.8*	5		2890.93 (9, 9)
40	2907.5	16	2908.1 (1, 4)	2908.57 (1, 6), 2908.80 (4, 6)

TABLE 1 (Continued)

S No.	Measured λ Å	Intensity Visual Estimate	λ , (u' , u'') Jevons	Identification λ Calculated (V' , V'')
41	2919.3*	2		2919.0 (10,10)
42	2928.2	1		
43	2944.5	2		
44	2952.1	4		
45	2961.8	20	2963.04 (0, 4)	2961.68 (3, 6), 2963.99 (0, 4)
46	2969.6*	5		2968.13 (9,10)
47	2978.0	6		
48	2988.9	30	2989.89 (1, 5)	2988.96 (4, 7), 2990.56 (1, 5)
49	3003.4	3		
50	3016.5*	10		3016.73 (5, 8), 3017.61 (2, 6)
51	3040.2	1		
52	3048.8	5	3048.76 (0, 5)	3048.8 (9, 11), 3049.76 (0, 5)
53	3053.4	16		
54	3075.5	25	3075.7 (1, 6)	3073.81 (7, 10), 3073.18 (4, 8) 3076.51 (1, 6)
55	3090.9	1		
56	3104.2	16	3103.1 (2, 7)	3104.31 (2, 7), 3103.4 (8, 11)
57	3122.5	12		
58	3132.4	4	3131.6 (3, 8)	3132.62 (3, 8)
59	3134.3*	4		3133.1 (9,12)
60	3139.0*	1		3138.58 (0, 6)
61	3148.0	1		
62	3158.3*	2		3160.6 (7, 11)
63	3166.1	12	3165.9 (1, 7)	3166.67 (1, 7)
64	3175.4	8		
65	3185.6	1		
66	3196.2	12	3194.3 (2, 8)	3195.26 (2, 8)
67	3221.0	30	3222.9 (3, 9)	3221.3 (9, 13), 3224.36 (3, 9), 3220.8 (6, 11)
68	3248.7*	8		3251.0 (7, 12), 3252.6 (10, 14), 3253.98 (4, 10)
69	3262.2*	6		3261.37 (1, 8)
70	3291.0	6	3289.7 (2, 9)	3290.76 (2, 9)
71	3299.6	1		
72	3304.9	1		
73	3304.4*	1		3313.6 (9, 14), 3314.8 (6, 12)
74	3320.8	15	3319.4 (3, 10)	3320.69 (3, 10)
75	3325.3*	20		3331.21 (0, 8)
76	3352.3*	15		3349.2 (4, 11)
77	3370.7	1		
78	3380.2*	6		3378.0 (8, 14), 3382.0 (5, 12)

TABLE 1 (Continued)

S No.	Measured λ \AA	Intensity Visual Estimate	λ , (u' , u'') Jevons	Identification λ Calculated (V' , V'')
79	3412.5*	1		3410.4 (9, 15), 3413.7 (6, 13)
80	3422.0*	4		3421.0 (3, 11)
81	3436.9*	6		3435.15 (0, 9)
82	3454.3	3		3453.3 (4, 12)
83	3463.4*	8		3465.72 (1, 10)
84	3473.1	0		
85	3484.7*	1		3485.2 (5, 13)
86	3491.8*	8		3496.8 (2, 11)
87	3519.2*	6		3517.6 (6, 14)
88	3549.1	2		
89	3558.7	3		
90	3581.2	2		
91	3592.8*	1		3593.5 (5, 14)
92	3610.5*	2		3608.2 (2, 12)
93	3638.6*	3		3640.8 (3, 13)
94	3669.72	2		
95	3682.0	1		
96	3700.0	2		
97	3732.8	2		
98	3776.7	2		
99	3794.4*	1		3793.3 (4, 15)
100	3812.7*	2		3815.8 (1, 13)
101	3826.0	2		
102	3860.0	1		

TABLE 2
THE UNIDENTIFIED BANDS

S No.	Measured λ Å	Intensity
1	2928.2	1
2	2944.5	2
3	2952.1	4
4	2978.0	6
5	3003.4	3
6	3040.2	1
7	3053.4	16
8	3090.9	1
9	3122.5	12
10	3148.0	1
11	3175.4	8
12	3185.6	1
13	3299.6	1
14	3304.9	1
15	3370.7	1
16	3473.1	0
17	3558.7	3
18	3581.2	2
19	3669.7	2
20	3682.0	1
21	3700.0	2
22	3732.8	2
23	3776.7	2
24	3826.0	2
25	3860.0	1

DISCUSSION

It has been mentioned earlier that no chemiluminescence was observed when germanium tetrachloride was mixed with atomic oxygen. This observation may be compared with the previous observations that the reactions of hydrocarbons with atomic oxygen are associated with chemiluminescence whereas the reaction of carbon tetrachloride with atomic oxygen is a non-luminous reaction [12].

Almost all bands on the more refrangible side of the spectrum belong to the D-X system of GeO. The D-X system of GeO was first studied by Shaw [6] and Sen Gupta [7] in emission from a carbon arc containing germanium compounds. Shaw [6] observed the bands from 2989Å and 2441Å region and Sen Gupta [7] extended their observations to 2342Å towards lower wavelength limit and to 3292Å towards higher wavelength. However, Jevons et al., [8] recognized the fact that to obtain greater contrast between band head and overlying structure of neighboring bands a source giving a lower temperature distribution would appear to be necessary. Consequently, they used an uncondensed discharge through a flowing mixture of GeCl₄ and oxygen and were able to extend the D-X band system of GeO to 3310Å region. However, in addition to GeO bands, they observed GeI lines, GeCl bands and a continuum. This is due to the non-selective excitation of spectra in electrical discharges. Due to the presence of different features in the spectra of electrical discharges, the observation of the weak features of the desired spectrum is difficult. This is also apparent from the published spectrogram of Jevons et al., [8]. On the other hand the excitation of spectra by chemiluminescent reaction is very selective and is comparatively free from the presence of other spectral features. Therefore, we have been able to extend the D-X system of GeO which is apparent from the large number of bands observed by us.

In addition to the bands belonging to the D-X system of GeO, there are several unidentified bands, which are given in Table 2. The spectra taken with a small quartz spectrograph shows a number of bands between 4000Å and 5100Å. However, these bands do not appear on the spectrogram taken with the 1.5 m grating spectrograph. This is understandable because the grating is blazed for 3000Å. However, the present observations indicate a strong possibility of a new band system in this region.

The possibility of a new band system of GeO in this region is indicated from the comparison of the observed band systems belonging to the diatomic oxides of the elements of the IV a group of the periodic table (CO, SiO, GeO, SnO and PbO). The energy level diagrams of these molecules and observed transitions are shown in Figure 4. (Only lower energy levels of CO are shown). Considering the regularity of vibrational constants and spectra, Barrow et al., [13] have concluded that the upper state of the D-X system of GeO corresponds to the D state of PbO and SnO molecules. $A \leftrightarrow X$, $B \leftrightarrow X$ and $C \leftrightarrow X$ systems on the longer wavelength side of $D \leftrightarrow X$ system have been observed

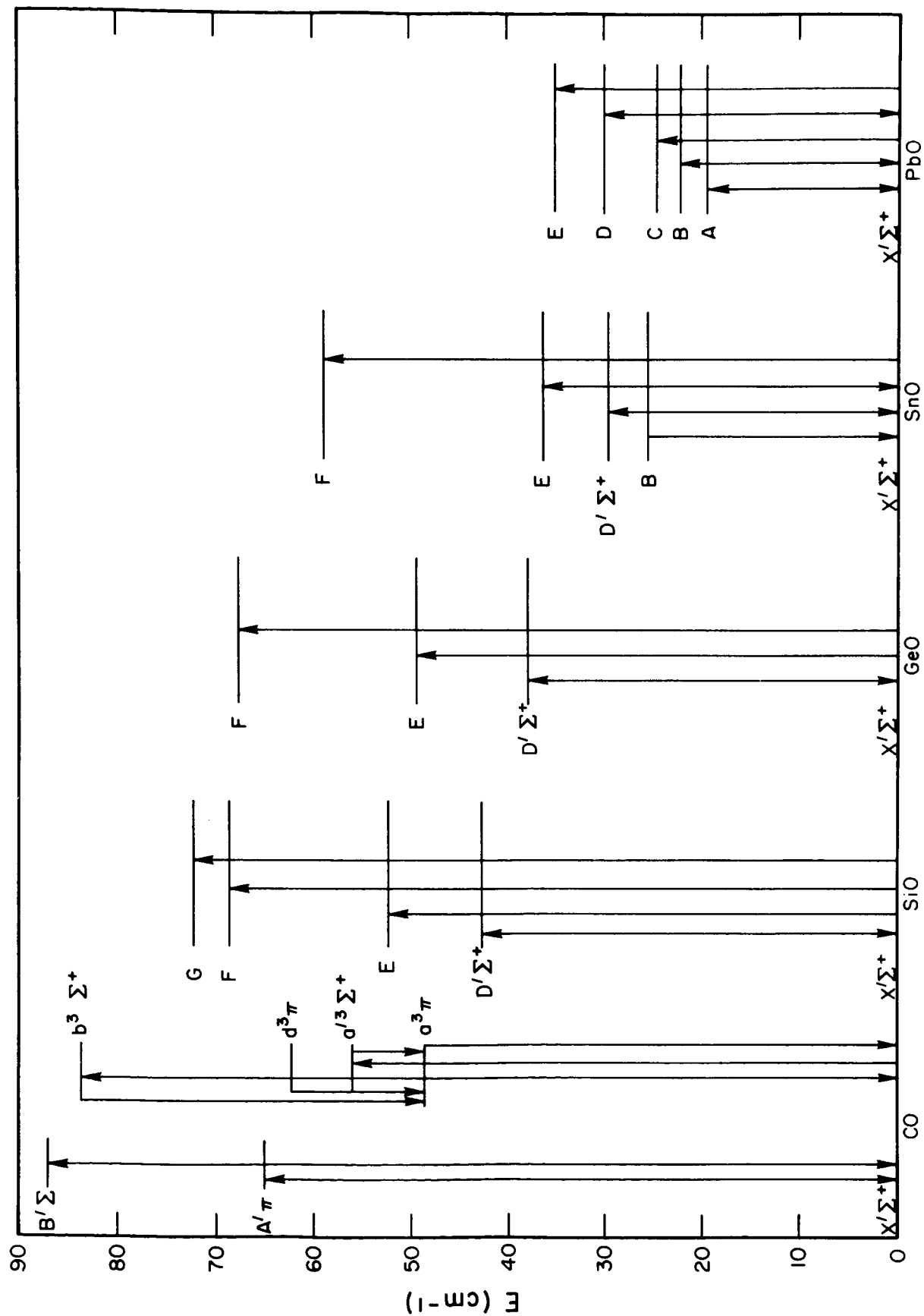


Figure 4. The energy level diagram and observed transitions of the monoxide of IVa group elements.

for the PbO molecule. In the spectrum of the SnO molecule a band system on the longer wavelength side of its D-X system has also been possibly observed [13]. The fact that no corresponding band systems are readily observed in the lighter molecules like SiO or GeO suggests that they may arise from a spin forbidden transition and may be observed in the corresponding state approaching Hund's case C. Since the GeO molecule is intermediate between the lightest and heaviest molecules of this group, the weak band system on the longer wavelength side of its D \leftrightarrow X system (analogous to PbO and SnO systems) may be expected.

It is therefore concluded that the study of chemiluminous reactions with atomic oxygen can give more spectroscopic information in some cases than available from conventional sources. The spectrum of the chemiluminescence produced during the reaction of germane and atomic oxygen should be investigated in greater detail, and particularly the region between 3000Å and 5000Å should be investigated for a possible new band system.

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